

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-093589

(43)Date of publication of application : 06. 04. 2001

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(51)Int. Cl. H01M 14/00  
H01L 31/04  
// C09B 5/62

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(54) OPTICAL SEMICONDUCTOR ELECTRODEPHOTOELECTRIC CONVERSION DEVICE AND PHOTOELECTRIC CONVERSION METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an optical semiconductor electrode of a high conversion rate stability and durability that may be readily fabricated at low cost.

SOLUTION: An optical semiconductor electrode may be obtained by a method comprising the steps of causing a solvent-soluble precursor of a solvent-insoluble pigment to adsorb to the surface of a semiconductor and reacting the precursor with at least one kind of primary amine to produce a photoelectric conversion layer of the solvent-insoluble pigment.

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### CLAIMS

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[Claim(s)]

[Claim 1] An optical semiconductor electrode being obtained by making a solvent soluble precursor of this solvent poorly soluble coloring matter react to at least one sort of the 1st class amine and having a photoelectric conversion layer by this solvent poorly soluble coloring matter on the surface of a semiconductor after making a solvent soluble

precursor of solvent poorly soluble coloring matter adsorb on the surface of a semiconductor.

[Claim 2] A solvent soluble precursor of solvent poorly soluble coloring matter 3,4,9,10-perylene tetracarboxylic acid In a 3,4,9,10-perylene monotetracarboxylic acid anhydride and a row. It is at least one sort chosen from a perylene derivative expressed with following general formula (I) and following general formula (II) The optical semiconductor electrode according to claim 1 which is at least one sort as which solvent poorly soluble coloring matter is chosen from a perylene pigment expressed with following general formula (III) a following general formula (IVa) a following general formula (IVb) and following general formula (V).

[Formula 1]

In said general formula (I)  $R^1$  expresses aliphatic series an aromatic hydrocarbon group or a heterocycle group and may be replaced by the substituent.

[Formula 2]

In said general formula (II) A expresses divalent aliphatic series an aromatic hydrocarbon group or a divalent heterocycle group and may be replaced by the substituent.

[Formula 3]

In said general formula (III)  $R^1$  and  $R^2$  express aliphatic series an aromatic hydrocarbon group or a heterocycle group and may be replaced by the substituent and may be mutually the same and may differ from each other.

[Formula 4]

In said general formula (IVa) and said general formula (IVb) A and B express divalent aliphatic series an aromatic hydrocarbon group or a divalent heterocycle group and may be replaced by the substituent and may be mutually the same and may differ from each other.

[Formula 5]

In said general formula (V) A expresses divalent aliphatic series an aromatic hydrocarbon group or a divalent heterocycle group and may be replaced by the substituent. R<sup>1</sup> expresses aliphatic series an aromatic hydrocarbon group or a heterocycle group and may be replaced by the substituent.

[Claim 3] The optical semiconductor electrode according to claim 1 or 2 whose semiconductor is at least one sort chosen from titanium oxide, tin oxide, tungstic oxide, zinc oxide, indium oxide, niobium oxide, nickel oxide, cobalt oxide and strontium titanate.

[Claim 4] A photoelectric conversion device which has at least a connecting means which connects an electrode of a couple contacted to an electrolyte and an electrode of this couple so that energization is possible and is characterized by at least one side of an electrode of this couple being the optical semiconductor electrode according to any one of claims 1 to 3.

[Claim 5] It is the photoelectric conversion method of contacting an electrode of a couple mutually connected so that energization was possible to an electrolyte and producing a photoelectric conversion reaction by irradiating at least one side of an electrode of this couple. A photoelectric conversion method that an electrode with which light is irradiated is characterized by being the optical semiconductor electrode according to any one of claims 1 to 3.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the optical semiconductor electrode to which solvent poorly soluble coloring matter is made to come to adsorb on the surface of a semiconductor, the photoelectric conversion device using it and the photoelectric conversion method.

[0002]

[Description of the Prior Art] In recent years use of sunlight attracts attention as an energy resource replaced with fossil fuels such as petroleum and coal. As a device which transforms light energy into electrical energy directly, the dry type solar cell in which pn junction was formed on inorganic semiconductor such as silicon and gallium arsenide is known well and it is put in practical use as a power supply of the object for remote places or a portable electronic device etc.

However conversion efficiency with these expensive solar cells is acquired.

On the other hand since the energy and cost which manufacture takes are very high there is a problem that it is difficult to use as an energy resource.

[0003] The wet solar cell which on the other hand used the photoelectrochemical reaction which occurs by the interface of a semiconductor and an electrolytic solution as an option which transforms light energy into electrical energy is known. As compared with the above-mentioned silicon gallium arsenide etc. semiconductors used here such as titanium oxide tin oxide and a zinc oxide can be manufactured at far low energy and cost and are expected as a future energy conversion material. However since a stable semiconductor like titanium oxide has the band gap as large as not less than 3 eV only about 4% of ultraviolet radiation of sunlight can be used and the way things stand high conversion efficiency cannot be expected.

[0004] On the surface of these semiconductors as a sensitizing dye then organic coloring matters such as cyanine dye and a xanthene dye (22'-bipyridyl) to make \*\*\*\*\* such as a ruthenium complex adsorb and to carry out spectral sensitization is tried (H. -- Tsubomura et al. Nature. 264 and 349 (1976).) Brian O'Regan Michael Gratzel Nature 353 736 (1991) JP1-220380A etc. However in the former there was a problem that the coloring matter which can stick to the surface of said semiconductor will be limited to coloring matter (solvent soluble pigment) meltable to solvent such as water thru/or an organic solvent.

[0005] On the other hand by carrying out vacuum deposition of the coloring matters such as phthalocyanine to a semiconductor surface, how to form the thin film of sensitizing dye is also learned -- \*\*\*\* (Calvin D. Jaeger-Fu-Ren Fan Allen J. Bard J. Am. Chem. Soc. 1980 and 102 2592.). In addition to the kind of coloring matter applicable also in this case being limited there was a problem of needing the special equipment for vacuum deposition. Therefore it is efficient and high durability and the actual condition is that the optical semiconductor electrode which can be manufactured cheaply the photoelectric conversion device using it and the photoelectric conversion method are not yet provided.

[0006]

[Problem(s) to be Solved by the Invention] This invention solves many problems in said former and makes it a technical problem to attain the following purposes. That is this invention can carry out available [ of the sunlight ] efficiently and is excellent in photoelectric conversion

efficiency, stability, endurance, etc., and an object of this invention is to provide the photoelectric conversion device and the photoelectric conversion method of excelling in photoelectric conversion efficiency using the optical semiconductor electrode which can be manufactured cheaply and easily and this optical semiconductor electrode.

[0007]

[Means for Solving the Problem] Said The means for solving a technical problem is as follows. Namely, after making a solvent soluble precursor of solvent poorly soluble coloring matter stick to the surface of <1> semiconductor, it is an optical semiconductor electrode being obtained by making a solvent soluble precursor of this solvent poorly soluble coloring matter react to at least one sort of the 1st class amine and having a photoelectric conversion layer by this solvent poorly soluble coloring matter on the surface of a semiconductor.

A solvent soluble precursor of <2> solvent poorly soluble coloring matter 3,4,9,10-perylene tetracarboxylic acid. In a 3,4,9,10-perylene monotetracarboxylic acid anhydride and a row. It is at least one sort chosen from a perylene derivative expressed with following general formula (I) and following general formula (II). Solvent poorly soluble coloring matter is an optical semiconductor electrode given in the above <1> which is at least one sort chosen from a perylene pigment expressed with following general formula (III), a following general formula (IVa), a following general formula (IVb), and following general formula (V).

[0008]

[Formula 6]

[0009] In said general formula (I),  $R^1$  expresses aliphatic series, an aromatic hydrocarbon group, or a heterocycle group and may be replaced by the substituent.

[0010]

[Formula 7]

[0011] In said general formula (II), A expresses divalent aliphatic series, an aromatic hydrocarbon group, or a divalent heterocycle group and may be replaced by the substituent.

[0012]

[Formula 8]

[0013] In said general formula (III)  $R^1$  and  $R^2$  express aliphatic seriesan aromatic hydrocarbon group or a heterocycle group and may be replaced by the substituent and may be mutually the same and may differ from each other.

[0014]

[Formula 9]

[0015] In said general formula (IVa) and said general formula (IVb) A and B express divalent aliphatic seriesan aromatic hydrocarbon group or a divalent heterocycle group and may be replaced by the substituent and may be mutually the same and may differ from each other.

[0016]

[Formula 10]

[0017] In said general formula (V) A expresses divalent aliphatic seriesan aromatic hydrocarbon group or a divalent heterocycle group and may be replaced by the substituent.  $R^1$  expresses aliphatic seriesan aromatic hydrocarbon group or a heterocycle group and may be replaced by the substituent.

<3> semiconductors are optical semiconductor electrodes given in the above <1> or <2> which is at least one sort chosen from titanium oxide, the tin oxide, tungstic oxide, zinc oxide, indium oxide, niobium oxide, nickel oxide, cobalt oxide and strontium titanate.

It has at least a connecting means which connects the electrode of the couple contacted to <4> electrolytes and the electrode of this couple so that energization is possible and at least one side of the electrode of this couple is a photoelectric conversion device characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <3>.

<5> The electrode of the couple mutually connected so that energization was possible is contacted to an electrolyte. By irradiating at least one side of the electrode of this couple it is the photoelectric conversion method of producing a photoelectric conversion reaction and the electrode with which light is irradiated is the photoelectric conversion method characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <3>.

[0018]

[Embodiment of the Invention] (Optical semiconductor electrode) The optical semiconductor electrode of this invention has a photoelectric

conversion layer by solvent poorly soluble coloring matter on the surface of a semiconductor. The optical semiconductor electrode of this invention is obtained by making the solvent soluble precursor of this solvent poorly soluble coloring matter react to at least one sort of the 1st class amine after making the solvent soluble precursor of solvent poorly soluble coloring matter adsorb on the surface of a semiconductor.

[0019]- semiconductor - As said semiconductor there is no restriction in particular and it can choose suitably according to the purpose for example titanium oxide, tin oxide, tungstic oxide, zinc oxide, indium oxide, niobium oxide, strontium titanate etc. are mentioned. These may be used by an one-sort independent and may use two or more sorts together. Especially in this invention the reasons of a photoelectric transfer characteristic, chemical stability, manufacture ease etc. to titanium oxide is preferred also in these.

[0020] About the shape of said semiconductor structure and a size there is no restriction in particular and it can choose suitably according to the purpose. For example as a structure of said semiconductor it may be the structure which consists only of this semiconductor and may be the structure in which the thin film layer of this semiconductor was formed on conductive base material such as plate such as transparent electrode such as ITO glass and Nesa glass, platinum, copper and black lead or a mesh electrode.

[0021]- Solvent soluble precursor of solvent poorly soluble coloring matter - the solvent soluble precursor of said solvent poorly soluble coloring matter It is a precursor of said solvent poorly soluble coloring matter and is a compound which dissolves in an aqueous solvent thru/or oily solvent such as water and alcohol easily. For example the perylene derivative etc. which are expressed with either 3,4,9,10-perylene tetracarboxylic acid, 3,4,9,10-perylene monotetracarboxylic acid anhydride, said general formula (I) and said general formula (II) are mentioned especially suitably.

[0022] As an example of a perylene derivative expressed with said general formula (I) the following compound (I-1 to I-10) is mentioned suitably.

[0023]

[Formula 11]

[0024] As an example of a perylene derivative expressed with said general formula (II) the following compound (II-11 - II-15) is mentioned suitably.

[0025]

[Formula 12]

[0026]- Adsorption of a solvent soluble precursor - Adsorption of said solvent soluble precursor to the surface of said semiconductor can be performed by dissolving this solvent soluble precursor in a solventpreparing a solution for exampleand making said semiconductor immersed into this solution.

[0027]As said solventalcoholic solvents such as methanolisopropyl alcohol ethylene glycol and methyl cellosolve water etc. are mentioned for example. When preparing said solution various alkalis acid etc. may be suitably added in said solvent by controlling pH of this solvent in order to maintain moderately the solubility of said solvent soluble precursor and adsorptivity to the surface of said semiconductor.

[0028]Said immersion may be performed under room temperature conditions and in order to promote adsorption it may carry out under conditions heated to temperature below the boiling point of a solvent if needed. After said immersion when said perylene derivative is used as said solvent soluble precursor after it is immersed into an acidic solution containing chloride acetic acid etc. and being washed by solvent such as water stoving of said semiconductor is carried out. As a result the surface of said semiconductor is adsorbed in said solvent soluble precursor and a thin film by this solvent soluble precursor is formed in it.

[0029]-Reaction with the 1st class amine - A reaction with the 1st class amine of said solvent soluble precursor by which the surface of said semiconductor was adsorbed can be performed by immersing this semiconductor into at least one sort of the 1st class amine or a solution containing at least one sort of the 1st class amine and making it react (for example heating). The 1st class diamine can also be contained outside the 1st class monoamine it can react to said solvent soluble precursor target solvent poorly soluble coloring matter can be generated in said the 1st class amine and the following compound (VI-1 - VI-28) should just specifically be suitably mentioned to it.

[0030]

[Formula 13]

[0031]

[Formula 14]



[0032]

[Formula 15]

[0033]

[Formula 16]

[0034]As conditions for said immersion and said reactionthere is no restriction in particular and it can choose suitably according to the purpose. As a result of said reactionsaid solvent soluble precursor changes to said solvent poorly soluble coloring matterand the photoelectric conversion layer by said solvent poorly soluble coloring matter is formed in the surface of said semiconductor.

[0035]- Solvent poorly soluble coloring matter -. [ whether said solvent poorly soluble coloring matter dissolves in an aquosity solvent thru/or organic solventssuch as waterand ] It is coloring matter which is hard to dissolveor after sticking to a semiconductor surface at leastit is hardly remelted coloring matterfor examplethe perylene pigment expressed with either following general formula (III)a following general formula (IVa)a following general formula (IVb) and following general formula (V) is mentioned suitably.

[0036]As an example of a perylene pigment expressed with said general formula (III)the following compound (III-1 - III-19) is mentioned suitably.

[0037]

[Formula 17]

[0038]

[Formula 18]

[0039]

[Formula 19]

[0040]As an example of a perylene pigment expressed with either said general formula (IVa) and said general formula (IVb)the following compound (IVa-1 - IVa-10 and IVb-1 - IVb-10) is mentioned suitably.

[0041]

[Formula 20]

[0042]

[Formula 21]

[0043]As an example of a perylene pigment expressed with said general formula (V) the following compound (V-1 to V-5) is mentioned suitably.

[0044]

[Formula 22]

[0045]- photoelectric conversion layer - Said photoelectric conversion layer is formed with said solvent poorly soluble coloring matter. Since said solvent poorly soluble coloring matter is excellent in chemical stability and endurance and is excellent in the holdout in the surface of said semiconductor and spectral sensitization can be carried out stably and efficient over a long period of time the optical semiconductor electrode of this invention which has this solvent poorly soluble coloring matter as a photoelectric conversion layer is excellent in efficiency high durability etc. In a wide range of fields the optical semiconductor electrode of this invention can be used conveniently and can be used especially conveniently for the following photoelectric conversion devices and photoelectric conversion methods of this invention.

[0046] (Photoelectric conversion device) A photoelectric conversion device of this invention may have at least a connecting means which connects an electrode of a couple contacted to an electrolyte and an electrode of this couple so that energization is possible and also may have a means of others suitably selected if needed.

[0047] Also in an electrode of said couple it is an optical semiconductor electrode of said this invention and another side is a counter electrode. As said counter electrode to oxidation and reduction if stable there will be no restriction in particular and according to the purpose it can choose from a publicly known thing suitably for example transparent electrode such as plate such as platinum gold and black lead ITO glass and Nesa glass etc. are mentioned.

[0048] A wire rod a plate a printed film or a vacuum evaporation film etc. which restriction in particular does not have as long as it has a function in which an electrode of said couple can be connected as said

connecting means so that energization is possible and consists of conductive materials such as a publicly known lead or various metal carbon and a metallic oxide is mentioned. This connecting means is connected to an electrode of said couple so that energization is possible.

[0049] As said electrolyte there is no restriction in particular and it can choose suitably according to the purpose. For example, salt such as potassium chloride, a lithium chloride and tetraethylammonium perchlorate. Nonaqueous solvent solutions such as acids such as alkalis such as sodium hydroxide and potassium carbonate, sulfuric acid and chlorides, these mixtures, these solutions or these alcohols and propylene carbonate etc. are mentioned. In this invention it is the purpose, such as attaining stabilization of the photoelectric current characteristic and a redox reagent which produces an oxidation-reduction reaction still more nearly reversibly [such as potassium iodide, iodine and p-benzoquinone] in said electrolyte may be added. A photoelectric conversion device of this invention can be used conveniently for a photoelectric conversion method of the following this inventions.

[0050] (A photoelectric conversion method) In a photoelectric conversion method of this invention an electrode of said couple mutually connected so that energization was possible is contacted to said electrolyte and a photoelectric conversion reaction is produced by irradiating at least one side of an electrode of this couple. [0051] In an electrode of said couple an electrode with which light is irradiated is an optical semiconductor electrode of said this invention and another side is said counterelectrode.

[0052] - In a photoelectric conversion device and a photoelectric conversion method of photoelectric conversion reaction - this invention a photoelectric conversion reaction arises as follows. That is, said optical semiconductor electrode and said counterelectrode are first immersed into said electrolyte (solution). This solvent poorly soluble coloring matter of said solvent poorly soluble coloring matter to said optical semiconductor electrode. Next, said general formula (III) In being at least one sort chosen from a perylene pigment expressed with either said general formula (IVa), said general formula (IVb) and said general formula (V) this few \*\*\*\* One sort. An exposure of white light or multicolor light which includes monochromatic light of an absorption wavelength region or one of its zones will transform such light energies into electrical energy.

[0053] According to a photoelectric conversion device and a photoelectric conversion method using a semiconductor electrode and this semiconductor

electrode of this invention. When it irradiates with 300-700-nm ultraviolet radiation thru/or visible light as a light with which it irradiates especially good photoelectric conversion efficiency is acquired -- semiconductor such as titanium oxide -- if independent it can use effectively to a wavelength band of visible light which cannot be used and luminous energy such as sunlight can be efficiently transformed into electrical energy.

[0054]

[Example] Hereafter although the example of this invention is described this invention is not limited to these examples at all.

[0055] (Example 1)

- 25 ml of semiconductor-alt. titanate acid tetraisopropyl was added gradually agitating violently in the mixed solution of 150 ml of pure water and the concentrated nitric acid 1.54g (specific gravity: 1.38). Temperature up was carried out to 80 °C continuing churning furthermore churning was continued at the temperature for 8 hours and the milky stable titanium oxide colloidal solution was prepared. This titanium oxide colloidal solution was condensed to 40 ml at 30 °C under decompression of 30 mmHg. Said titanium oxide colloidal solution was coated with the spin coat method on the glass substrate (the following "ITO glass substrate" is called) with which the layer of ITO was covered and was calcinated at 500 °C for 1 hour. This operation was repeated 3 times and the titanium oxide layer about 1.0 micrometer thick was formed on the ITO glass substrate. When the crystal structure of the obtained titanium oxide membrane was checked with the X-ray diffraction method it was a mixture of an anatase and a rutile type. The ITO glass substrate which supported said titanium oxide layer was used as said semiconductor.

[0056]- Adsorption of a solvent soluble precursor - The 3,4,9,10-perylene tetracarboxylic anhydride 1g as said solvent soluble precursor was distributed in 100 ml of water and 1 g of sodium hydroxide was added it stirred at 80-90 °C for 1 hour and the dark red solution was obtained. After having added about 1 ml of acetic acid in this solution having adjusted pH to 6-7 and said ITO glass substrate was immersed at 50-60 °C for 1 hour it is immersed into about 0.1 M of dilute hydrochloric acid and water and after methanol subsequently washed reduced pressure drying was carried out at about 50 °C.

[0057]- Said semiconductor was immersed after formation-desiccation of solvent poorly soluble coloring matter into 100 ml of 1-chloronaphthalenes which dissolved 0.5 ml of beta-phenethylamine (said illustration compound VI-7) and 1 ml of acetic acid which are said the

1st class amine and it was made to react at about 150 °C under a nitrogen air current for 4 hours. After ending reaction and this semiconductor -- acetone -- subsequently methanol washed and reduced pressure drying was carried out at about 50 °C for 1 hour.

[0058] When the ultraviolet and visible absorption spectrum of the photoelectric conversion layer formed in the surface of said semiconductor was measured (drawing 3) it was checked that this photoelectric conversion layer is an adsorption film by the perylene pigment (said illustration compound III-7) which is said solvent poorly soluble coloring matter. By the above the photoelectric conversion layer by said perylene pigment (said illustration compound III-7) produced the optical semiconductor electrode which comes to carry out adsorption formation on the surface of said semiconductor.

[0059] Next the lead was connected to the layer portion of ITO covered by the glass substrate. The terminal area of said lead covered and adhered with the epoxy resin. The optical semiconductor electrode was produced by the above.

[0060] Drawing 1 is an approximate account figure for explaining the produced optical semiconductor electrode. The optical semiconductor electrode 1 has the layer 3 of ITO, the titanium oxide layer 4 and the photoelectric conversion layer 5 by said perylene pigment (said illustration compound III-7) on the glass base material 2 at this order. The terminal area of the layer 3 of ITO and the lead 7 was covered with the epoxy resin as the adhesive agent 6 and has adhered with it. In this terminal area the lead 7 is accommodated into the glass tube 8.

[0061] Drawing 2 is an approximate account figure for explaining the photoelectric conversion method using the photoelectric conversion device provided with said optical semiconductor electrode. Here a saturated calomel electrode \*\* is immersed in a platinum electrode as the optical semiconductor electrode 1 and the counter electrode 9 which were produced and is immersed into the inside of the transparent glass cell 13 and the electrolytic solution 11 as the reference electrode 10. The electrolytic solutions 11 are 0.1M-sodium sulfate / 0.02M-potassium iodide solution. It is connected to the potentiostat 12 via the lead 7 as a connecting means and energization of each electrode is attained.

[0062] In this photoelectric conversion device it is held so that the potential of the optical semiconductor electrode 1 might be set to 0V to the reference electrode 10 and it is irradiated with white light (the xenon lamp of 500W illumination 4000lux) from the back side of the optical semiconductor electrode and the value of the photoelectric current at

this time was measured with the potentiostat. The measurement result was shown in Table 1.

[0063] (Example 2) In Example 1 the outside which the following performed through "adsorption of - solvent soluble precursor -" and "formation of - solvent poorly soluble coloring matter -" produced the optical semiconductor electrode and the photoelectric conversion device like Example 1 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 1.

[0064]- Adsorption of a solvent soluble precursor - said semiconductor After distributing in the solution which dissolved 0.5 g of N-(4-carboxyethyl)-3,4,9,10-perylene tetracarboxylic acid-3,4-imide (said illustration compound I-3) as said solvent soluble precursor in 100 ml of sodium carbonate solution 1% and making it immersed at about 50 °C for 1 hour It is immersed into about 0.1 M of dilute hydrochloric acid and water and after methanol subsequently washed reduced pressure drying was carried out at about 50 °C.

[0065]- Said ITO board was immersed after formation-desiccation of solvent poorly soluble coloring matter into 100 ml of 1-chloronaphthalenes which dissolved 1 g of o-phenylenediamines (said illustration compound VI-20) which are said the 1st class diamine and it was made to react at about 200 °C under a nitrogen air current for 4 hours. after ending reaction and this ITO board -- acetone -- subsequently natural seasoning was washed and carried out with methanol.

[0066] When the ultraviolet and visible absorption spectrum of the photoelectric conversion layer formed in the surface of said semiconductor was measured (drawing 4) it was checked that this photoelectric conversion layer is an adsorption film by the perylene pigment (said illustration compound V-5) which is said solvent poorly soluble coloring matter. By the above the photoelectric conversion layer by said perylene pigment (said illustration compound V-5) produced the optical semiconductor electrode which comes to carry out adsorption formation on the surface of said semiconductor.

[0067] (Comparative example 1) In Example 1 the outside which did not perform "adsorption of - solvent soluble precursor -" and "formation of - solvent poorly soluble coloring matter -" produced the optical semiconductor electrode and the photoelectric conversion device like Example 1 enforced the photoelectric conversion method and measured photoelectric current. The measurement result was shown in Table 1.

[0068] (Comparative example 2) In Example 1 adsorption of - solvent soluble precursor - and "formation of - solvent poorly soluble coloring matter -" are not performed After said semiconductor is immersed in the

solution which dissolved 50 mg of 2457-tetraiodofluorescein and disodium salts in 50 ml of ethanol solutions at 70-80 °C for 1 hour. Methanol, water and the outside that acetone and methanol subsequently washed and carried out natural seasoning are examples. The optical semiconductor electrode and the photoelectric conversion device were produced like 1. The photoelectric conversion method was enforced and photoelectric current was measured. The measurement result was shown in Table 1.

[0069] (Comparative example 3) In Example 1, adsorption of - solvent soluble precursor - and "formation of - solvent poorly soluble coloring matter -" are not performed. After said semiconductor is immersed at 180-190 °C for 1 hour into the liquid which distributed 50 mg of perylene pigments (said illustration compound III-7) in 50 ml of 1-methyl-2-pyrrolidone. The outside which acetone washed and was dried is an example. The optical semiconductor electrode and the photoelectric conversion device were produced like 1. The photoelectric conversion method was enforced and photoelectric current was measured. The measurement result was shown in Table 1.

[0070]

[Table 1]

[0071]

[Effect of the Invention] According to this invention, available [ of the sunlight ] can be carried out efficiently. It excels in photoelectric conversion efficiency, stability, endurance, etc. and the photoelectric conversion device and the photoelectric conversion method of excelling in photoelectric conversion efficiency can be provided using the optical semiconductor electrode which can be manufactured cheaply and easily and this optical semiconductor electrode.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] Drawing 1 is an approximate account figure of the optical semiconductor electrode of this invention.

[Drawing 2] Drawing 2 is an approximate account figure for explaining the photoelectric conversion method using the photoelectric conversion device provided with the optical semiconductor electrode of drawing 1.

[Drawing 3] Drawing 3 is an ultraviolet and visible absorption spectrum

of the optical semiconductor electrode of Example 1.

[Drawing 4] Drawing 4 is an ultraviolet and visible absorption spectrum of the optical semiconductor electrode of Example 2.

[Description of Notations]

- 1 Optical semiconductor electrode
  - 2 Glass substrate
  - 3 The layer of ITO
  - 4 Titanium oxide layer
  - 5 Photoelectric conversion layer
  - 6 Adhesive agent
  - 7 Lead
  - 8 Glass tube
  - 9 Counterelectrode
  - 10 Reference electrode
  - 11 Electrolytic solution
  - 12 Potentiostat
  - 13 Transparent glass cell
-